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John R. Smith

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Delphi
5725 Delphi Drive
Troy, MI 48098-2815

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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
USAF, AFRL
AF Office of Scientific Research
875 North Randolph Street
Rm 3112
Arlington, VA 22203
Joan Fuller

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13. SUPPLEMENTARY NOTES
This final report describes the portion of the MEANS2 work done at Delphi. The third and final year of the contract was transferred to UCSB (Professor Anthony Evans).

14. ABSTRACT The hot-section turbine components of aircraft engines can depend on a thermally-grown, thin alpha-alumina layer for corrosion and oxidation protection. This thermal processing can leave a continuous layer of gamma-Ni(Al) adjacent to the oxide. Since the oxide must remain adherent upon thermal cycling, it is essential to quantify the factors affect adhesion at the gamma-Ni(Al)/alpha-alumina interface. We have previously shown that this adhesion is sensitive to the stoichiometry or atomic termination of the interface and that this stoichiometry depends on the Al activity in the Ni(Al). It was required then to determine the temperature and Al concentration dependence of the Al activity in Ni(Al).This was done via first principles, density functional theory. Results indicate that the Al activity can vary by 14 orders of magnitude over a temperature range 400 K < T < 1700 K. We find the interface stoichiometry to be Al-rich, but located near the stoichiometric phase on the phase diagram. Software we developed for activity compuations is available on request.

15. SUBJECT TERMS
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Final technical report for Delphi component of MEANS2: Knowledge oriented materials engineering of layered thermal barrier systems (NOMELT)

Work began on the Delphi part of the NOMELT program on 15 April, 05, contract no. FA9550-05-C-0039, as monitored by Dr. Joan Fuller and Dr. Timothy Harr of the Air Force Office of Scientific Research. The Delphi part of this work concluded in January, 07. The work currently is continuing at the University of California, Santa Barbara. This is the final report for the Delphi portion of the program. Attention is called to the following attachments: Standard Form 298, Physical Review B **74**, 224110 (2006), and Scripta Materialia **55**, 1147 (2006).

The subject of our work is the performance and durability of rotor blade materials found in hot-section components of aircraft engines. In particular we are concerned with the durability under thermal cycling of thermally-grown oxides (TGO) on these materials. The TGO are grown to provide corrosion and oxidation protection for the rotor blades. Durability in turn is dependent on adequate adhesion of the oxides to the underlying blade.

The TGO is grown on a Ni(Al) bond coat. The latter is applied to the rotor blade surface. The TGO grows via Al segregation to the surface, combining with oxygen to form alumina, Al_2O_3. Then the interface that must have adequate adhesion is $Ni(Al)/Al_2O_3$. We have found that adhesion is sensitive to the stoichiometry (ratio of number of Al atoms to O atoms) of the interface. In turn, this stoichiometry depends on the Al activity. Activity measurements are limited in number and in the available temperature range.

So the need for a reliable means of computing the Al activity of Al in Ni solution (Ni(Al)), became apparent. Our overall goal is to provide to the Air Force a software capability to compute Al activities for these materials and environments. Over the years, we have developed a capability for carrying out first-principles, density-functional computations, which have been rather thoroughly tested for accuracy and reliability. This application presented new challenges, however, because of the need for relatively high temperatures T over 1000 C. This meant that we have to include temperature dependences of enthalpy and entropy up to these high temperatures. For this, we must compute vibrational (phonon) energetics for dilute solutions of Al in Ni.

We found (see attached Physical Review B **74**, 224110 (2006), and Scripta Materialia **55**, 1147 (2006), a substantial temperature dependence of both enthalpies and entropies. In fact, these temperature dependencies were in opposite directions. The entropy temperature dependence was found to be larger than that of the enthalpy. As a result, the Al activity was determined to have a substantial temperature dependence,

varying by 14 orders of magnitude over the temperature range 100 C < T < 1400 C. The predicted Al activities agreed well with available experimental data. We had previously computed interfacial phase diagrams for $Ni(Al)/Al_2O_3$. Those diagrams, coupled with our new knowledge of the Al activity, allow us to determine that the interface is in an Al-rich phase, with the stoichiometric phase near by. This means that we must consider the adhesion of both Al-rich and stoichiometric phases. Adhesion computations for those phases are underway. Effects of impurities and additives such as S, Pt, and Hf on the adhesion are also being considered.

The software we developed to do these activity computations will is available to the Air Force upon request.